Methodology for Derivation of Pesticide Water Quality Criteria for the Protection of Aquatic Life

Phase II: Methodology Development and Derivation of Chlorpyrifos Criteria

Prepared for the Central Valley Regional Water Quality Control Board

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Executive Summary

The goal of this project is to develop a methodology for derivation of pesticide water quality criteria for the protection of aquatic life in the Sacramento River and San Joaquin River basins. The project will be accomplished in three phases. Phase I (TenBrook & Tjeerdema 2006) was a comparison of existing methodologies. This is a report of the results of Phase II, in which a new methodology is developed. Phase III will be to apply the new methodology to derive criteria for up to five pesticides including diazinon and chlorpyrifos, two organophosphate insecticides of particular concern in the Sacramento River watershed due to listings under 303(d) of the federal Clean Water Act.

This report is organized into four chapters. The first is an introduction to this phase of the project with a discussion of the approach taken to develop the new methodology. The second chapter is an evaluation and selection of methods for inclusion in the new methodology. Twelve pesticide data sets, including a chlorpyrifos set collected according to procedures in the new methodology, were used to evaluate various techniques. Particular attention was given to the assessment of distributional assumptions used in species sensitivity distribution (SSD) methods, and to determination of appropriate duration and frequency components of criteria statements. Results of these evaluations, together with findings from the Phase I report, were used to select elements to include in the new methodology. For criteria derivation with small data sets, Chapter 2 includes derivation of assessment factors, based on existing pesticide data, as well as derivation of a default acute-to-chronic ratio (ACR) for use when chronic data are lacking.

Chapter 3 presents the new methodology in a step-by-step format. Major features include: guidance for collection, evaluation, and reduction of data; a SSD method to derive criteria when five or more data are available; an assessment factor (AF) method to derive acute criteria when fewer than five acute toxicity data are available; an ACR method to derive chronic criteria when fewer than five chronic data are available; methods for assessing bioavailability; methods for assessing compliance in cases of mixtures of chemicals with similar modes of toxic action and for mixtures that exhibit non-additive toxicity; methods for quantifying relationships between toxicity and water quality parameters, such as pH and temperature; techniques for assessing whether derived criteria might harm particularly sensitive species, lead to bioaccumulation, harm ecosystems, harm threatened and endangered species, or lead to unacceptable levels of pesticides in other environmental compartments. Finally, a template is given for how to state final criteria in terms of magnitude, duration and frequency. The appendices include flow charts for data collection and criteria derivation processes, a blank data summary sheet, and tables of data sources, physical-chemical test methods, data rating schemes, critical values for assessing outliers, assessment factors, and examples of quantitative structure activity relationships.

In Chapter 4 the new methodology is used to derive acute and chronic criteria for chlorpyrifos. Although this was originally part of Phase III of the project, it was included

here to facilitate review of the proposed methodology. Using data sets collected, evaluated, and reduced according to guidance in Chapter 3, the SSD method was used to derive an acute criterion and the ACR method was used to derive a chronic criterion. An ACR of 2.2 was calculated for chlorpyrifos. The appendices include tables of data rated acceptable for criteria derivation or for use as supporting information, as well as data summary sheets for all studies rated acceptable for criteria derivation. The final acute and chronic criteria for chlorpyrifos were both 10 ng/L. These values are lower than the USEPA chlorpyrifos acute and chronic freshwater criteria of 83 and 41 ng/L, respectively (USEPA 1986). They are also lower than current water quality objectives for the lower San Joaquin, Sacramento and Feather Rivers and the Sacramento-San Joaquin River Delta (CVRWQCB 2009). Acute and chronic objectives for both of these water bodies are 25 and 15 ng/L, respectively. A detailed comparison was done of the data sets used to derive the three different chlorpyrifos criteria above and of the results using different calculation methods. Differences between established values and those derived by the new methodology are primarily attributed due to differences in the data sets used to derive them. The new criteria data sets include data points from studies conducted since the older criteria and objectives were derived, and exclude data points that were used in prior derivations, but did not pass the data evaluation scheme developed for the new methodology. It is important to note that four acute values in the new data set are below the USEPA criterion of 0.083 μg/L.

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List of acronyms and abbreviations

ACE	Acute-to-Chronic Estimation
AChE	Acetylcholinesterase
ACR	Acute to Chronic Ratio
AF	Assessment Factor
ANZECC	Australia and New Zealand Environment and Conservation Council
APHA	American Public Health Association
ARMCANZ	Agriculture and Resource Management Council of Australia and New Zealand
ASTM	American Society for Testing and Materials
BAF	Bioaccumulation Factor
BCF	Bioconcentration Factor
BMF	Biomagnification Factor
BSAF	Biota Sediment Accumulation Factor
CAS	Chemical Abstract Service
CCME	Canadian Council of Ministers of the Environment
CDFG	California Department of Fish and Game
CEAM	Center for Exposure Assessment Modeling
CEMC	Canadian Environmental Modeling Center
CSIRO	Commonwealth Scientific and Industrial Research Organization, Australia
CVRWCB	Central Valley Regional Water Quality Control Board
CWA	Clean Water Act
DHM	Dissolved Humic Material
DOC	Dissolved Organic Carbon
DOM	Dissolved Organic Matter
DPR	Department of Pesticide Regulation
EC_x	Concentration that affects x% of exposed organisms
ECB	European Chemicals Bureau
EU	European Union
EXAMS	Exposure Analysis Modeling System
FACR	Final Acute to Chronic Ratio
FAV	Final Acute Value
FCV	Final Chronic Value
FDA	Food and Drug Administration
FIFRA	Federal Insecticide Fungicide and Rodenticide Act
GMAV	Genus Mean Acute Value
HC_x	Hazardous Concentration potentially harmful to x% of species
IC_x	Inhibition concentration; concentration causing *x*% inhibition
ICE	Interspecies Correlation Estimation
IUPAC	International Union of Pure and Applied Chemistry
K	Interaction Coefficient
K_H	Henry's law constant
K_{ow}	Octanol-Water partition coefficient
K_p or K_d	Solid-Water partition coefficient
LC_x	Concentration lethal to *x*% of exposed organisms

LD_x	Dose lethal to *x*% of exposed organisms
LFER	Linear Free Energy Relationship
LOEC	Lowest Observed Effect Concentration
LOEL	Lowest Observed Effect Level
MATC	Maximum Acceptable Toxicant Concentration
MHSPE	Ministry of Housing, Spatial Planning and the Environment
NOEC	No Observed Effect Concentration
OECD	Organization for Economic Co-operation and Development
QSAR	Quantitative Structure Activity Relationship
pK_a	Acid dissociation constant
RIVM	National Institute of Public Health and the Environment, Bilthoven, The Netherlands
RPF	Relative Potency Factor
SETAC	Society of Environmental Toxicology and Chemistry
SMACR	Species Mean Acute to Chronic Ratio
SMAV	Species Mean Acute Value
SSD	Species Sensitivity Distribution
TBT	Tributyltin
TCE	Time Concentration Effect
TE	Toxic Equivalent
TEF	Toxic Equivalency Factor
TES	Threatened and Endangered Species
TFM	3-trifluoromethyl-4-nitrophenol
TGD	Technical Guidance Document
TMDL	Total Maximum Daily Load
TSD	Technical Support Document for Water Quality-based Toxics Control
TTE	Time To Event
TU	Toxic Unit
US	United States
USEPA	United States Environmental Protection Agency

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